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Professor Kruger

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Stanford Univ Jr
651 Serra Street Rm 260
Stanford, CA 94305-4125

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**Visible/Near-IR Optical Parametric Oscillator System
for Kinetic Studies of Nonequilibrium Air Plasmas
using Cavity Ring-Down Spectroscopy**

Grant # F49620-98-1-0331

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Submitted to
Dr. Robert Barker
Air Force Office of Scientific Research/NE
801 N. Randolph Street, Room 732
Arlington VA 22203-1977

by

Professor Charles H. Kruger (PI)
Department of Mechanical Engineering
Thermosciences Division
Stanford University
Stanford, California 94305-3032

and

Professor Richard N. Zare (co-PI)
Department of Chemistry
S. G. Mudd, Rm. 133
Stanford University
Stanford, California 94305-5080

May 31, 1999

Mechanical Engineering Department
Stanford University
Stanford, California 94305

Visible/Near-IR Optical Parametric Oscillator System for Kinetic Studies of Nonequilibrium Air Plasmas using Cavity Ring-Down Spectroscopy

1. Introduction

In March 1998, Prof. Charles H. Kruger and Prof. Richard N. Zare were awarded a Department of Defense University Research Instrumentation Program (DURIP) grant (Grant # F49620-98-1-0331) for the purchase of a Visible/Near-IR Optical Parametric Oscillator system for kinetic studies of nonequilibrium air plasmas. The grant period was from 03/01/98 to 02/28/99. The present final technical report details the equipment purchased under this grant and summarizes the research purposes of this equipment.

2. Equipment Purchase Information and Status

The DURIP grant funds of \$122,000 were used in conjunction with \$14,103 of institutional non-federal cost-sharing funds to purchase a Continuum Optical Parametric Oscillator (OPO) system. This system comprises a Powerlite 8000 Nd:Yag laser system, a DS-1 temperature stabilized second and third harmonic generator and output, a SL-500 injection seeder, and a Sunlite2 visible OPO/Amplifier. In addition, funds from separate sources in the amount of \$26,016.98 were used to purchase a FX-1 frequency doubler in order to extend the system's capabilities to the ultraviolet spectral range. The OPO system was ordered on March 25, 1999 and delivered to Stanford University on August 30, 1999. The complete system is paid in full and all funds from the present DURIP grant have been expended.

3. New research projects with the new system

3.1. Background

The newly acquired OPO system will provide support for research on creating and sustaining atmospheric pressure air plasmas with electron number densities greater than 10^{13} cm^{-3} , in the framework of our current MURI "Air Plasma Ramparts" program (Grant number AF-F49620-97-1-0316) under the direction of Dr. Robert Barker. In this research, nonintrusive and sensitive measurements of the temperature and concentration profiles of both trace (electrons, positive and negative ions, radicals) and major (N_2 , O_2 , N , O) species are required in order to determine accurate reaction rates for the kinetic processes controlling ionization and electron recombination. In addition, these measurements are also useful to monitor the effectiveness of various excitation schemes for generating low temperature (300-2000 K) air plasma ramparts with electron number densities on the order of 10^{13} cm^{-3} .

These measurements will be accomplished by the resonant absorption spectroscopy technique of Cavity Ring-Down Spectroscopy (CRDS), using the newly acquired tunable, pulsed OPO laser system. The CRDS technique offers both the high sensitivity and resolution needed for the measurements envisaged. Its implementation will be greatly facilitated as the new OPO laser affords continuous spectral coverage over a wide range (225 nm to 1.68 μm), very high spectral resolution (less than 0.1 cm^{-1} , a critical factor 2 or 3 times better than conventional narrowband lasers), and high energies in nanosecond pulses (from 50 mJ in the visible to 5 mJ in the near-infrared and UV).

More specifically, the new OPO system will be applied to the measurement of temperatures and concentrations using the following species:

- NO from its $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) transition band at 226 nm, within the minima of the overlapping $B^3\Sigma^- \leftarrow X^3\Sigma^-$ bands of molecular oxygen,¹
- O_2 from its $B^3\Sigma^- \leftarrow X^3\Sigma^-$ transitions in the UV,
- N_2^+ from its $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ (0,0) transition band at 391 nm,
- NO and NO^+ from their infrared overtones between 1.2 and 1.5 μm ,
- N and O from the NO $C^2\Pi - A^2\Sigma^+$ (0,0) transition band at 1.22 μm , since the NO $C^2\Pi$ state population, as a result of predissociation and its inverse, is in partial equilibrium with the N and O species,² and
- O_2^- , from its $A^2\Pi_u \leftarrow X^2\Pi_g$ (0,0) transition band near 400 nm. The concentration of this species is of particular importance as electron attachment in an electronegative gas such as air can greatly reduce electron concentrations below the desired $10^{13}/\text{cm}^{-3}$.

Rotational and vibrational temperatures of species absorbing within the output spectrum of the laser will also be measured. In particular, NO has intense UV absorption bands issued from the ground state. Since the UV is a very dense spectral region, in order to make unambiguous measurements, CRDS with the very narrow linewidth OPO laser source will be employed to measure spectral line intensities thanks to its sub-Doppler spectral resolution.

For electron density measurements we plan to develop a measurement of Stark broadening of the H_β transition at 486 nm using the narrow linewidth OPO source for CRDS, in order to obtain sub-Doppler lineshapes limited only by collisional broadening.

3.2. Proof of concept experiments

It was originally planned to start applying the new OPO laser in proof-of-concept CRDS measurements of species concentrations produced by the 50 kW radio-frequency (RF) plasma torch of the High Temperature Gasdynamics Laboratory at Stanford. The RF torch environment is usually considered to be hostile to laser diagnostics for several reasons. One is the large amount of radiated RF noise that affects the electronics of lasers and associated detection equipment. Other difficulties more directly associated with the use of the CRDS technique in air plasmas include thermal lensing effects due to the strong temperature gradi-

ents at the plasma edges, spurious absorption by species produced by the plasma (in particular ozone or NO_2), and degradation of the transmissivity of the CRDS cavity mirrors as a result of the intense UV radiation produced by the air plasma. Due to a delay in delivery of the OPO system, this first series of experiments was not conducted with the OPO but instead with an existing conventional dye laser available in our laboratory. Although our dye laser can only provide access to a limited spectral range, it was possible to use it to probe the concentrations of N_2^+ from the (0-0) band of the first negative system in the range 387-392 nm. Although N_2^+ is only a minor participant in the reaction pathways that govern electron number densities, it serves as an excellent candidate for determining the feasibility of employing CRDS in the hostile environment of an air plasma. The results, summarized below, demonstrate that the CRDS technique can indeed be applied in the hostile RF torch environment and gives confidence that the new OPO system, with its a much wider spectral range of operation than the dye laser, will enable us to greatly expand the number of species available for spectroscopic interrogations in the plasma torch.

3.2.1. Description of the CRDS technique

Cavity ring-down spectroscopy is a laser-based direct absorption technique capable of probing ground and excited-state populations in hostile environments.³⁻⁵ Using CRDS, it is possible to obtain spatially-resolved concentration and temperature profiles of dilute gas-phase species. In pulsed CRDS, a laser source injects a pulse of light into a high-finesse optical resonator, the ring-down cavity (RDC), which is formed by two high-reflectivity mirrors. The intensity of the light initially trapped within the RDC decays exponentially owing to losses within the RDC which include scattering and transmission by the cavity mirrors as well as absorption of light by gas-phase species present within the cavity. The decay time constant, τ , for light trapped in the RDC is given by:⁶

$$\tau = t_r / (2 [(1 - R) + \alpha L_s]),$$

where t_r is the round-trip time of a light pulse in the cavity, R is the reflectivity of the cavity mirrors, and L_s is the sample pathlength. The absorbance of a sample placed in the RDC is then found from the relation:⁴

$$\alpha L_s = 0.5 t_r (1/\tau - 1/\tau_o),$$

where τ_o is the decay constant of the empty cavity. Experimentally, τ is determined by measuring the intensity of light leaking from the RDC through the second cavity mirror. An absorption spectrum of gas-phase species present in the RDC is generated by plotting the decay rate of light within the RDC, which is proportional to $1/\tau$, as a function of wavelength.

The inherent sensitivity of the CRDS technique is a result of the insensitivity of τ to fluctuations in the intensity of the light source which limit the sensitivity of other direct absorption techniques. Furthermore, the light pulse traverses the optical cavity many times resulting in effective pathlengths which exceed the sample length by thousands of times.

3.2.2. CRDS measurements of N_2^+ concentrations in air plasmas

We describe below the application of CRDS to probe the concentration of N_2^+ in an atmospheric-pressure air plasma at 7000 K. This represents the first attempt to utilize CRDS to detect trace species in a plasma where severe thermal lensing, caused by large temperature gradients, is expected. In what follows we identify the major noise sources which limit the sensitivity of the technique, and briefly outline future experiments that apply CRDS to indirectly probe electron number densities of low temperature nonequilibrium air plasmas.

3.2.3. Experimental

Figure 1 shows a schematic of the CRDS apparatus. A Nd:YAG pumped dye laser is used to generate light between 387.0 and 392.0 nm using Exalite 392A dye. Pulses of light from the dye laser (8-12 mJ/pulse, 8 ns duration) are mode matched to the RDC using a pair of lenses (5.0 cm focal length) and a pinhole (0.25 mm). The RDC, which is 2.1 m in length, is comprised of two high reflectivity mirrors (Los Gatos Research, $R = 0.9993$) mounted to an aluminum rail 3 m in length. The rail may be translated, allowing the RDC axis to sample different portions of the air plasma. A turning prism is also mounted to the rail, which deflects the beam into the RDC. By carefully aligning the beam parallel to the translation axis of the rail, before the turning prism, the RDC may be translated across the plasma orifice (7 cm in diameter) while maintaining alignment between the laser and the RDC. Baffles (0.6 cm orifice) are mounted in the RDC to reduce the background light intensity at the detector and to protect the cavity mirrors from the large amount of ultraviolet radiation generated by the air plasma. Light exiting the cavity is deflected by a mirror (also mounted to the translating rail) onto a fast photomultiplier located several meters from the second mirror. Photocurrent generated by the photomultiplier is digitized using a digitizing oscilloscope (Gage, 6012f). A personal computer is used to fit the decay waveforms to an exponential function and extract $1/\tau$, while stepping the dye laser through a wavelength range of interest. Emission spectroscopy was performed in parallel with the CRDS measurements to provide an independent measurement of plasma temperature.

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Krug/Zare
Stanford University

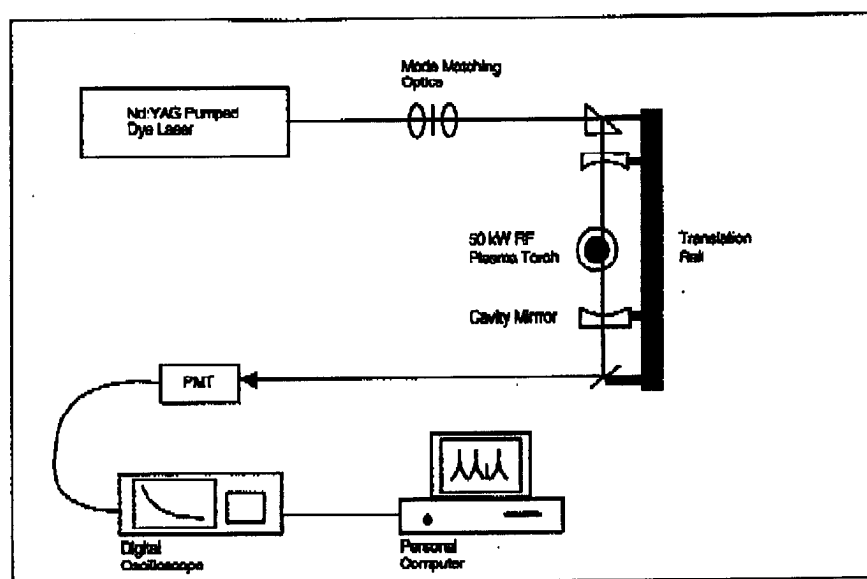


Figure 1. Schematic diagram of CRDS setup used to probe N_2^+ in an equilibrium air plasma

3.2.4. Results

Figure 2 shows the absorption spectrum of N_2^+ , obtained with the ring-down cavity aligned with the center of the air plasma, 1.0 cm above the plasma torch head, along with the predicted absorption spectrum generated with the line-by-line radiation code NEQAIR2.⁷ The temperature of the air plasma, determined independently via emission spectroscopy, was approximately 7000 K. Each spectral element represents an average of 10 decay rates, each obtained by fitting a waveform that was itself an average of 25 single-shot waveforms.

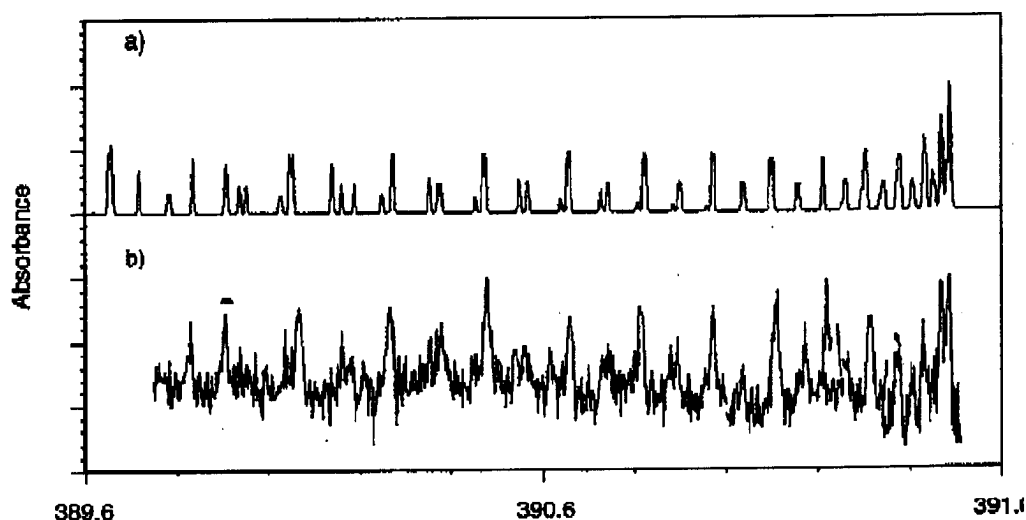


Figure 2. (a) Predicted and (b) experimental CRDS spectra of N_2^+ in a 7000 K air plasma.

With the RF plasma torch off, τ_0 is typically 10 μ s. With the RF plasma on, however, τ_0 decreases to 0.65 μ s, even with the cavity translated 2.5 cm beyond the edge of the plasma torch orifice. This decrease in τ_0 is attributed to two loss mechanisms within the RDC. First, there exists a long-lived gas-phase species generated by the plasma torch, possibly O_3 or NO_2 , which possesses a broad featureless absorption feature in the wavelength region of interest. The concentration of this background absorber fluctuates in the turbulent air surrounding the plasma causing shot-to-shot fluctuations in τ . These fluctuations decrease the sensitivity of the absorption measurement, and increase in severity as the cavity is translated toward the edge of the plasma where the laser beam samples more of the surrounding air. Currently, we are exploring methods to purge the turbulent region surrounding the plasma without perturbing the plasma itself. The second source of noise is caused by irradiation of the dielectric mirrors by UV radiation from the air plasma. UV-induced reduction in the reflectivity of dielectric mirrors has been observed previously,⁸ and was attributed to deformation of the top dielectric layer after absorption of UV photons with energies of a few eV. The effect of UV radiation on the reflectivity of the dielectric mirrors used in the study outlined here was examined by translating the RDC well outside of the air plasma and shielding the mirrors from radiation from the plasma. A 50% increase in τ_0 was observed when the mirrors were shielded from the plasma torch. Rapid recovery of R is observed when the RF torch is extinguished. Therefore, fluctuations in the intensity of UV radiation from the RF torch produces fluctuations in τ . This second source of noise is most acute when probing the center of the air plasma and decreases as the cavity is translated toward the edge of the plasma.

Figure 3 shows an expanded view of the N_2^+ absorption spectrum showing the rotational bandhead obtained experimentally and the predicted absorption spectrum generated with NEQAIR. The width of the absorption feature generated by NEQAIR was broadened to match the width of the observed absorption feature. The intensity of the predicted transition is then in excellent agreement with that obtained experimentally.

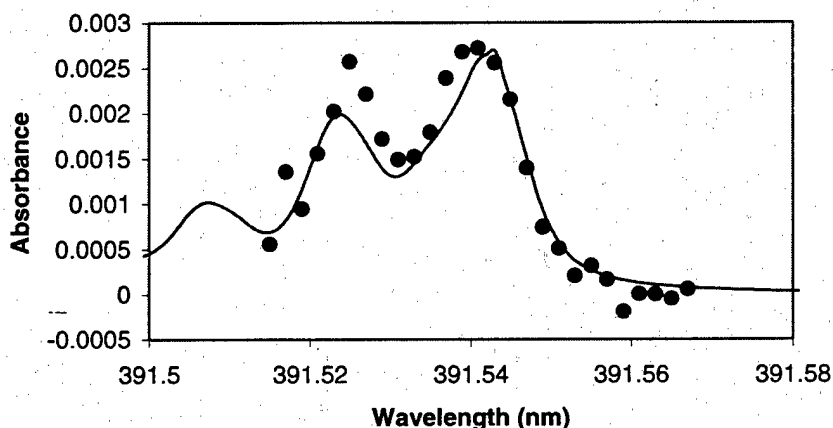


Figure 3. Experimental (points) and Simulated (line) absorption spectrum of the N_2^+ bandhead.

A spatial profile of the concentration of N_2^+ was obtained by measuring the absorption by N_2^+ at 391.6 nm as the RDC was translated from the center of the plasma torch to the edge of the plasma orifice. Optical losses caused by absorption of N_2^+ as a function of distance from the center of the plasma are shown in figure 4a. The losses from N_2^+ were probed at 0.2 cm intervals with a spatial resolution of 0.5 mm, the average laser beam diameter over the plasma orifice. The increase in uncertainty in the determination of the optical losses near the edge of the plasma is caused by the absorbing background gasses in the turbulent air surrounding the plasma mentioned earlier. The CRDS technique measures line-of-sight integrated losses within the air plasma. An Abel transform was employed to extract absorption losses of N_2^+ as a function of radial distance from the center of the plasma from the optical loss data. Using the absorption cross section obtained from NEQAIR2, these losses were used to calculate the absolute concentration of N_2^+ as a function of radial distance (see figure 4b). These N_2^+ concentrations are in excellent agreement with the N_2^+ concentrations calculated from the plasma temperature profile which was obtained by measuring the integrated absolute intensity of the O triplet at 777.3 nm. For the present experimental conditions, it is expected that the plasma is close to LTE and therefore the measured N_2^+ concentrations can be related to electron number densities using chemical equilibrium relations. Electron number densities obtained in this manner are shown in Fig. 5.

3.2.5. Conclusion

We have demonstrated the ability of CRDS to probe the concentration of a trace species present within an equilibrium air plasma at 7000 K. A preliminary spatially resolved concentration profile of N_2^+ was obtained, and noise sources limiting the sensitivity of the measurement have been identified. We are currently exploring methods to increase sensitivity. Future investigations involving N_2^+ include probing both rotational and vibrational temperature profiles of N_2^+ , as well as N_2^+ concentration as a function of plasma temperature. As yet, thermal lensing of the laser beam by the plasma has not been identified as a major source of loss within the RDC. Additional species concentration measurements will be greatly facilitated by using the newly acquired OPO system.

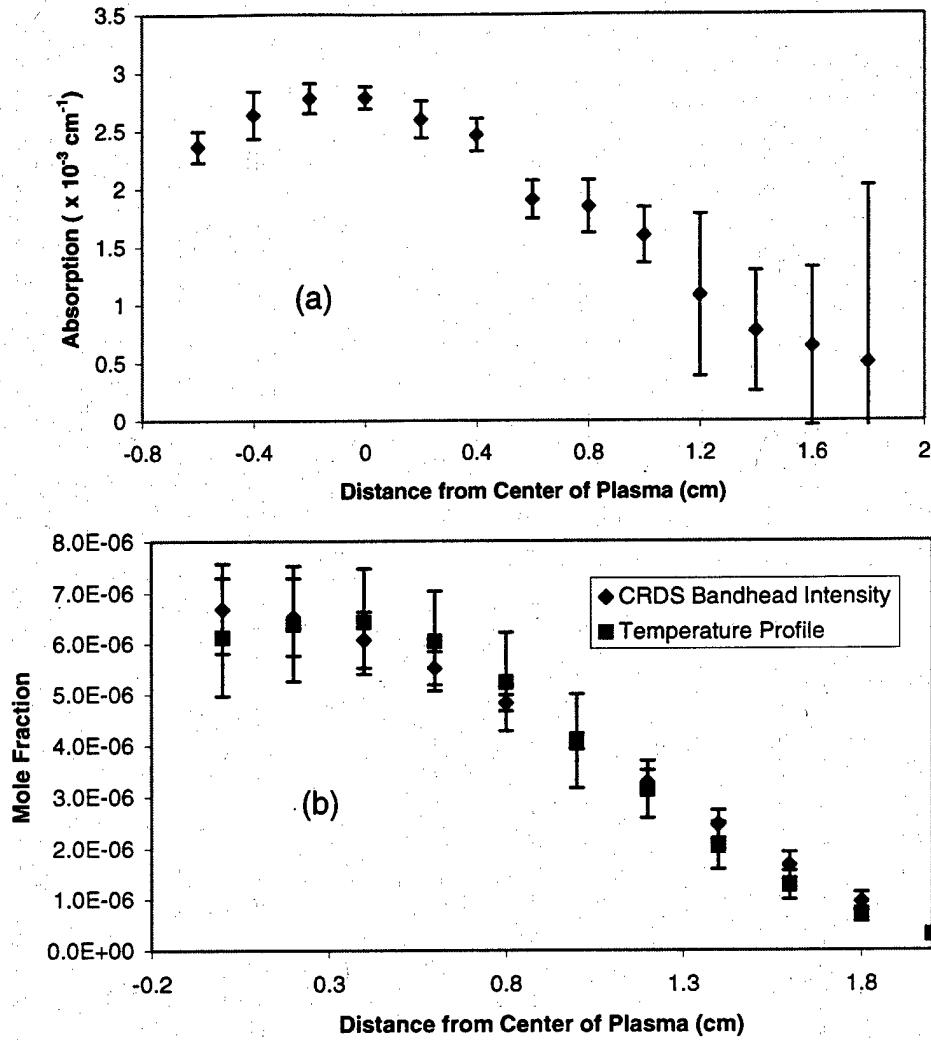


Figure 4. a) Spatially resolved absorbance profile of N_2^+ in an equilibrium air plasma at 7000K. b) Concentration profile of N_2^+ obtained by Abel inversion of absorbance profile.

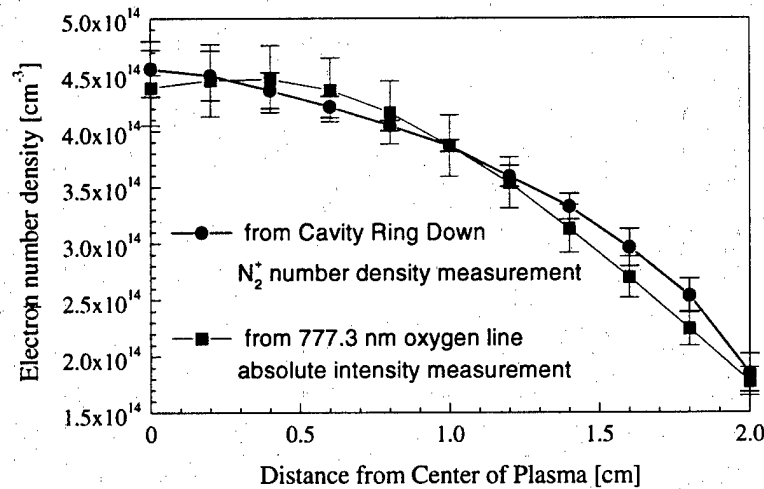


Figure 5. Electron number density profiles inferred using LTE relations from measured ground state N_2^+ concentrations and from measured excited atomic oxygen populations.

4. Program impact on current and future scientists

The following is a list of current graduate students and co-workers whose research will benefit from the new OPO system.

Mechanical Engineering:

Mr. Richard J. Gessman, Ph.D. Student
Dr. Christophe O. Laux, Research Associate
Dr. Thomas G. Owano, Senior Research Scientist
Mr. Denis Packan, Ph.D. Student
Mr. Hugh T. Stinnette, Ph.D. Student
Mr. Edward H. Wahl, Ph.D. Student
Ms. Lan Yu, Ph.D. Student
Mr. Maosheng Zhao, Ph.D. Student

Chemistry Department:

Dr. Uwe Lommatzsch, Post-Doctoral Fellow
Dr. Barbara A. Paldus, Post-Doctoral Fellow
Dr. Thomas Spence, Post-Doctoral Fellow

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